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CHEMICAL LASER RESEARCH

Glen P. Perram, Major, USAF

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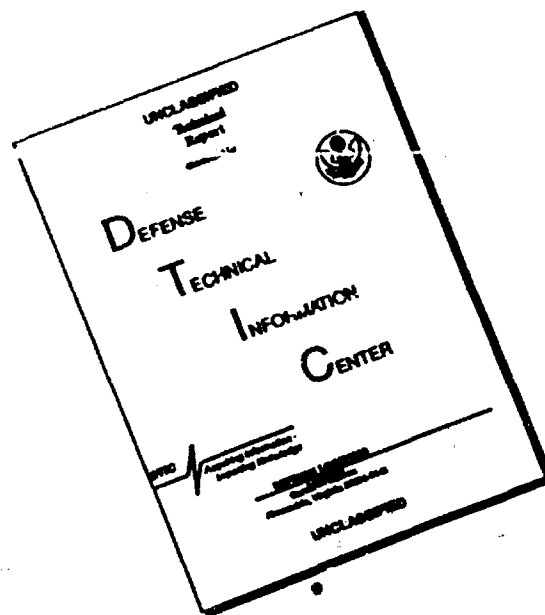
May 1993

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## I. Introduction

High power short wavelength chemical laser (SWCL) systems offer great advantages for strategic and tactical military applications, including both weapons and imaging missions. The promise of very high brightness, high mass efficiency and wavelength agility has justified a modest basic research program for more than a decade. Along the way, a great deal has been learned about energetic, state-selective chemistry at high reagent densities.

Significant progress towards the demonstration of a visible chemical laser has been made during the past few years. Highly efficient methods of chemically producing metastable electronic states at concentrations exceeding  $3 \times 10^{16}$  molecules/cm<sup>3</sup> have been developed. Energy transfer from these metastables to suitable lasing species has been used to demonstrate gain in the visible. Chemically generated gain of 0.029 %/cm on the (A-X) electronic transition in bismuth fluoride has been demonstrated using pulsed thermolysis of fluorine azide and trimethylbismuth mixtures. Recently, a table-top shock tube facility has been used to achieve unsaturated lasing in the same system.

During the past ten years, over 400 articles and reports have resulted from this research program. The current scientific goals of this research program include: (1) investigation of dynamical constraints which lead to chemical production of specific electronically excited states, (2) kinetic studies of radical/radical and excited state/excited state interactions, (3) quantum resolved ro-vibrational energy transfer within both ground and excited electronic states, (4) synthesis of both novel energetic compounds and suitable lasing precursors, (5) fluid dynamic studies of reactive mixing, and (6) development of novel, inexpensive laser hardware. This bibliography summarizes this Department of Defense sponsored research on Short Wavelength Chemical Lasers since 1980.

## II. Why Short Wavelength Chemical Lasers?

### A. Historical Perspectives

Many of the earliest chemical lasers<sup>1,5</sup> were based on the establishment of an inversion between vibrational states as proposed by J.C. Polanyi in 1965.<sup>6</sup> Exothermic reactions, liberating their energy into the stretching of newly formed chemical bonds can provide both complete and partial vibrational inversions. After Cool and Stevens<sup>7</sup> demonstrated an HF laser requiring no electrical input, high power, highly efficient chemical lasers were envisioned.<sup>7</sup> HF lasers with powers exceeding 1 MW have been demonstrated and are in an advanced state of development.<sup>8</sup> These infrared devices are inherently high gain lasers with significant diffraction limited beam divergence. Recently, efficient HF overtone lasers have also been demonstrated.

To achieve lasing in the visible portion of the spectrum, the higher energies of excited electronic states are required. The early photolytic iodine laser<sup>9</sup> led to a search for a chemical means of exciting atomic iodine. The shortest wavelength high power chemical laser in existence today is the Chemical Oxygen-Iodine Laser (COIL) which operates on the  $5^2P_{1/2} - 5^2P_{3/2}$  transition in atomic iodine at 1.315  $\mu\text{m}$ .<sup>10</sup> These lasers are driven by resonant energy transfer from metastable singlet oxygen. While chemical oxygen-iodine lasers are in the early stages of large scale development, a 25 kW device has been tested at the Air Force's Phillips Laboratory and scaling to high output power devices with excellent beam quality is under active investigation.<sup>8</sup>

Early attempts to demonstrate a short wavelength chemical laser were based on analogy to HF/DF lasers where a chemical reaction is used directly to excite an upper laser level. Research during the 1970's on candidate systems such as BaO have been reviewed elsewhere.<sup>11,308</sup> These early efforts failed in

large part because the reaction chemistry was not constrained to efficiently produce a single electronically excited state. The current Short Wavelength Chemical Laser program addresses this issue by investigating highly energetic chemical reactions which are constrained by spin conservation rules to efficiently generate excited metastable species. These metastable species then act as a large reservoir of chemical energy which may be efficiently transferred to a suitable lasing molecule.

#### B. Missions and Performance Potential

In light of the availability of several high power chemical lasers, why should we invest in the development of a visible chemical laser? There are several compelling answers to this question which depend on the anticipated application.

Short Wavelength Chemical Lasers (SWCLs) have great potential as highly efficient, wavelength agile, deployable, high brightness laser systems. Applications of such devices include: (1) directed energy weapons for both tactical and strategic military missions, (2) military imaging and diagnostic missions such as illuminators, optical radars, beacons, and atmospheric compensators, (3) naval communications, and (4) nuclear fusion drivers. Laser sources provide a high degree of control over the wavelength, bandwidth, directionality, polarization, and temporal characteristics of radiation for diagnostic purposes. Indeed, the field of diagnostic spectroscopy has been revolutionized by tunable laser sources.<sup>12</sup>

The electronic state transitions of visible lasers promise greater mass efficiency,  $\sigma$ , and significantly greater brightness on target,  $B$ , than the previous generation of high power, vibrational chemical lasers such as HF, CO, and CO<sub>2</sub>. The higher energy stored per molecule in electronic states provides for laser output energies per mass of input reactants on the order of

$\sigma$  - 1 MJ/kg. These efficiencies are important for space based missions to the extent that the required payload mass is driven by chemical reagents. Theoretical values for mass efficiency can easily be calculated from the energy content per molecule, but are often substantially reduced by the diluent gas flows required to control thermal conditions of the laser. Mass efficiency is also driven by reagent stoichiometry and key reaction branching ratios.

The ability of a laser to damage a distant target is often characterized by the source brightness which depends on the laser output power, beam divergence, beam jitter, optical quality of the beam and other parameters. The flux delivered to the target is reduced by beam divergence. This beam divergence is controlled by diffraction at the limiting aperture and thus, the delivered beam flux depends inversely on the square of the laser wavelength. This strong advantage for shorter wavelengths can be realized only if the pointing and tracking optics establish a low value for beam jitter on the target. Atmospheric turbulence can significantly increase beam divergence above the diffraction limit, but may be compensated by adaptive or nonlinear optics. It is clear that short wavelength lasers provide a strong enhancement in brightness. For example, an NF/BiF(A-X) laser operating in the blue would provide a factor of 30-40 increase in intensity over an equivalent power HF laser.

Several additional parameters that characterize the performance of laser devices are nozzle power flux,  $\delta$ , small signal gain,  $\gamma$ , and beam quality, BQ. The nozzle power flux is a measure of energy in the flow and is a primary scaling parameter. Values for  $\delta$  provide information on the needed nozzle flow area for a given laser output power. It is the need for large nozzle power fluxes that drives chemical lasers to supersonic flow operation. Small signal gain is important for several reasons: (1) it establishes a lower bound for the gain length, (2) large gains may imply difficulties with amplified

spontaneous emission (ASE), parasitics, multi-mode operation, and extraction length, (3) low gains imply high intra-cavity fluxes, long cavity mode build-up times and high-Q optical resonators, and (4) designs for the optical resonator are based on  $\gamma$ . Visible chemical lasers tend toward high nozzle flux and low gain.

Atmospheric propagation is highly favorable in the visible portion of the spectrum. Candidate visible chemical laser systems operate near the peak transmission and COIL devices operate in a narrow transmission window. The ultraviolet cut-off at about  $0.36 \mu\text{m}$  is due to ozone absorption. The poor transmission near  $1.4 \mu\text{m}$  is due to water absorption and is a less severe problem in the upper atmosphere. The transmission at very short wavelengths is partially degraded by aerosol and Rayleigh scattering.

Visible chemical lasers utilizing diatomic molecules as the lasing medium provide a great deal of wavelength tunability due to the large number of vibrational and rotational states. Indeed, quasi-continuous tunability of as much as 100 nm may be achievable. This attribute may be particularly important for imaging missions where counter-measures may be wavelength dependent and where discrimination against an intense source at nearby wavelengths is required. The very high sensitivity of detectors operating in the visible, namely photomultiplier tubes, make visible lasers highly desirable for imaging missions.

While some SWCL concepts are inherently pulsed, most of the research efforts have focused on those systems with potential for scaling to high CW powers. The CW devices offer a high duty cycle, good thermal kill characteristics, and low peak energy flux through the atmosphere. Pulsed operation may be desirable for some imaging missions and might be achieved with magnetic effects similar to those being investigated for COIL devices.

### C. Requirements, Concepts and Approaches

The above characteristics of visible chemical lasers provide high payoff for the development of this new class of laser device. They also imply great constraints to potential systems. To develop an efficient, scalable, high brightness laser system operating in the visible under chemical excitation is indeed a difficult problem.

Chemically driven visible lasers may be divided into several classes according to the excitation mechanism. Several examples include: (1) direct chemical lasers based on analogy to HF, (2) energy transfer chemical lasers based on analogy to COIL, (3) pulsed, detonation driven chemical lasers, (4) optically driven chemical lasers where a very intense, explosively driven light source is used as the excitation source, (5) frequency doubled COIL and (6) hybrid electro-chemical lasers where electrical power is used to initiate highly exothermic reactions.

Early attempts to demonstrate a visible chemical laser were based on analogy to HF/DF lasers where a chemical reaction is used directly to excite an upper laser level. These early efforts failed in large part because the reaction chemistry was not constrained to efficiently produce a single electronically excited state. The high density of electronic states accessible with these highly exothermic reactions necessarily requires some reaction selectivity to insure efficient production of an upper laser level. The current SWCL program addresses this issue by investigating highly energetic chemical reactions which are constrained by spin conservation rules to efficiently generate excited metastable species. These metastable species then act as a large reservoir of chemical energy which may be efficiently transferred to a suitable lasing molecule. Some metastable energy carriers that can be efficiently produced are listed in Figure 1.

<u>Metastable Energy Carrier</u>	<u>Energy (eV)</u>	<u>Obtained Energy Density</u>	<u>Lasant Transition</u>	<u>Lasant Lifetime (<math>\mu</math>s)</u>	<u>Wavelength (nm)</u>
$O_2(a^1\Delta)$	0.98	16 J/l	IF(B-X)	7.0	625
$NF(a^1\Delta)$	1.4	6.7 J/l	BiF(A-X)	1.4	450
			NF(b-X)	23,000	530
			IF(B-X)	7.0	625
$NCl(a^1\Delta)$	1.1	5.5 J/l	IF(B-X)	7.0	625
$N_2(A^3\Sigma)$	6.2	0.1 J/l	IF(B-X)	7.0	625
			SO(A-X)	35	299
			NO(A-X)	0.2	248

Figure 1. Efficiently produced metastable energy carriers.

A three-fold approach to demonstrating a visible chemical laser based on this energy transfer concept is being pursued: (1) development of highly efficient chemical generators of energetic metastable species, (2) identification of potential laser species with the required spectroscopic and kinetic properties, and (3) coupling of a suitable metastable generator to a lasant and the demonstration of a scalable visible chemical laser. Figure 2 presents a flow chart embodying this approach. A generic reaction mechanism for this energy transfer concept is shown in Figure 3.

Identification and characterization of potential lasant species usually involves several different studies including spectroscopy, lasant production kinetics, radiative and collisional dynamics of excited and ground electronic states, and optically pumped laser demonstrations. Optically pumped lasers are particularly useful in studying the kinetics under approximated chemical laser conditions." Producing a metastable energy reservoir involves basic kinetic studies of highly energetic reactions and scaling of reagents to engineer a small scale metastable generator. These activities must be coordinated to insure the development of a complete system with efficient coupling of the metastable and lasant. Energy transfer excitation studies, examination of pressure scaling laws, and chemical compatibility studies are included in this phase.

Based on the system performance criteria discussed above, the physical constraints for proposed visible chemical laser systems are rigorous. An exothermic reaction involving lightweight molecules with a near unit branching of products to a single, excited electronic state is required to chemically drive the laser. The reaction barrier should be moderately low so as the rate for product formation is rapid, yet the reagents are acceptably stable. The energy transfer chemical laser must also identify a suitable lasant molecule which efficiently and rapidly receives energy from the metastable reservoir.

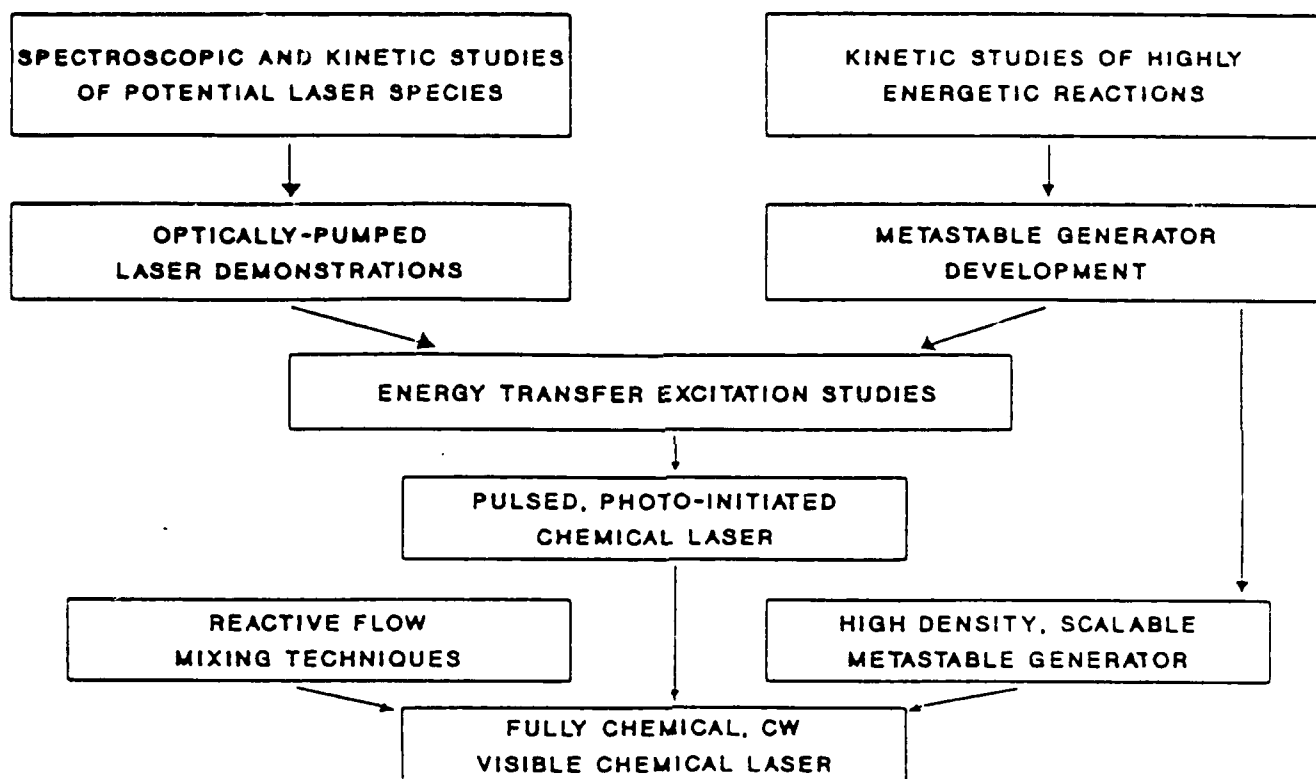
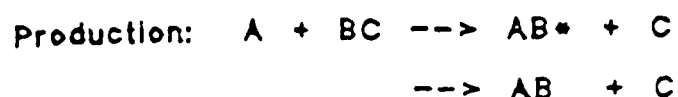


Figure 2. Approach to developing a visible chemical laser based on energy transfer.

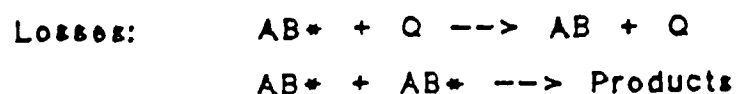
## Metastable Energy Reservoir



Branching to Excited  
Products



$\tau \approx \text{seconds}$

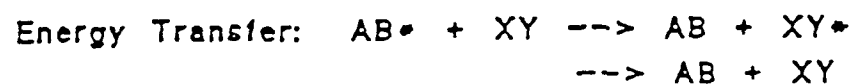


Quenching  
Pooling

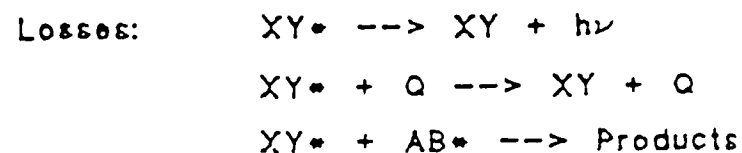
## Lasant Production and Excitation



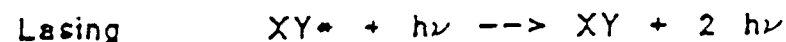
XY Lasant Ground State



Efficiency of Transfer



Radiation  
Quenching  
Pooling



Stimulated Emission

Figure 3. Metastable Energy Transfer Mechanism

The rate of chemically pumping the lasant must be of the order  $10^{19}$  molecules/cm<sup>3</sup>-sec and critical inversion densities are typically  $10^{13}$  molecules/cm<sup>3</sup>. Near unit efficiency in the energy transfer is required for efficient operation and all energy loss mechanisms ultimately result in thermal control problems.

Typically, the metastables are transported from a chemical generator to a nozzle assembly where they are mixed with the lasant molecule. Excited state - excited state interaction must be minimal to prevent significant losses upon pressure scaling. Singlet excited states are desirable in this regard, since their paired electrons tend to be non-reactive. Moderate radiative lifetimes for the lasant molecule are desirable. Lifetimes shorter than 1-10  $\mu$ s imply mixing requirements which are currently unattainable. Thus, visible chemical lasers are typically low gain systems.

The lasant molecule should have rapid rotational and vibrational thermalization processes to pool all the energy into a few ro-vibrational states. These processes are shown schematically in Figure 4. The lasant should suffer few quenching, dissociation, and other losses during the thermalization. In order to maintain an unpopulated ground state, the ground electronic state should be highly reactive, repulsive, or substantially displaced in equilibrium internuclear position. Typically, the lasant concentration is low compared to the concentration of metastables and the lasant makes many excitation/stimulated emission cycles to extract the full energy in the flow. In this way, the mass of the lasant does not significantly affect the laser mass efficiency.

Gas temperature should be low to maintain a maximum gain and prevent rotational dilution. Supersonic expansions aid in controlling temperature. In order to best use the fluid dynamic cooling, most heat of reaction should be deposited in the flow prior to expansion.

## Electronic Transitions in Diatomic Lasants

CHEMICAL  
EXCITATION OR  
ENERGY TRANSFER  
FROM CHEMICALLY  
EXCITED SPECIES

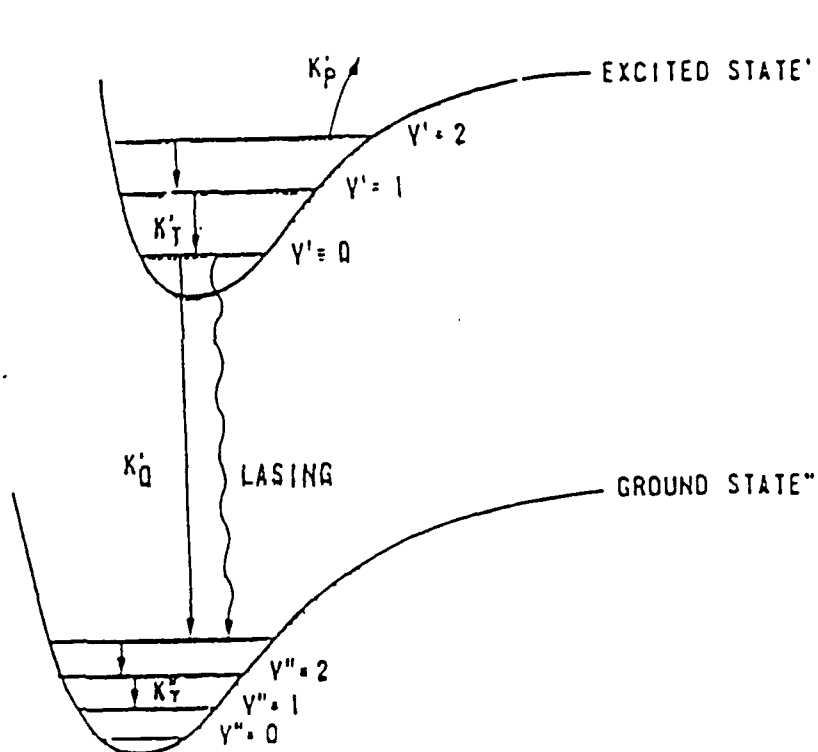


Figure 4. Chemical laser relaxation kinetics.

Reagent preparation can be a difficult task for some visible chemical lasers. Low vapor pressures, thermodynamically unstable reagents, and highly reactive reagents are often encountered. Methods of scaling and delivering these species can present significant chemical engineering problems.

A laser demonstration is challenging and requires the integration of chemical kinetics, reactive mixing, and optical physics. While the scientific and engineering problems are formidable, a few promising SWCL systems including the excited NF driven laser have been identified and characterized. A survey of potential SWCL systems is provided in the next section.

### III. Candidate Short Wavelength Chemical Laser Systems

Several candidate SWCL systems based on energy transfer are summarized in Figure 5. The metastable energy carriers and their experimentally obtained energy densities are indicated. Efficient means of extracting the energy via lasing are indicated by the lasing molecule options. These systems span the full wavelength range from 0.25 - 0.91  $\mu\text{m}$ .

The first excited electronic state of nitrogen fluoride,  $\text{NF}(a^1\Delta)$ , is the premier candidate for a metastable energy carrier to drive a visible laser. Energy densities of greater than 6.7 J/l have been demonstrated. The production chemistry is compatible with existing HF laser hardware and lasing could be achieved in the blue near  $\lambda=450$  nm.  $\text{NF}(a^1\Delta)$  can be chemically generated with near unit efficiency, is highly immune to pooling and quenching energy loss mechanisms, and possesses a reactive ground state.

The potential energy curves for NF are shown in Figure 6. NF is iso-electronic with molecular oxygen and has an analogous structure. There are only three electronic states at energies less than 5 eV. This feature significantly reduces the pathways for energy partitioning during production and subsequent transport of  $\text{NF}(a)$ . The potential energy curves reported in Figure 6 were computed by H. Michaels. Note that the electronic states X, a, and b have nearly identical equilibrium internuclear separations. The singlet states correlate to excited nitrogen atoms,  $\text{N}(^2\text{D})$ .

Efficient, chemical production of  $\text{NF}(a^1\Delta)$  has been demonstrated using several different chemistries. Clyne and White were the first to observe a chemiluminescent reaction between H and  $\text{NF}_2$  that produced both  $\text{NF}(a-X)$  and  $\text{NF}(b-X)$  emissions.<sup>13</sup>

<u>Lasant</u>	<u>Excitation Mechanism</u>
BiF(A-X)	$NF(a) + Bi \rightarrow NF + Bi(^2D)$ $NF(a) + Bi(^2D) \rightarrow BiF(A) + N$
NF(b-X)	$NF(a) + I^* \rightarrow NF(b) + I$
IF(B-X)	$NF(a) + IF(X,v) \rightarrow NF(X) + IF^+$ $IF^+ + NCl(a)/O_2 \rightarrow IF(B) + NCl/O_2$
BH(A-X)	$NF(a) + BH(X) \rightarrow NF(X) + BH(a)$ $NF(a) + BH(a) \rightarrow NF(X) + BH(A)$
$I(^2P_{1/2} - ^2P_{3/2})$	$NCl(a) + I \rightarrow NCl(X) + I^*$
NCl(b-X)	$NCl(a) + I^* \rightarrow NCl(b) + I$
Na( $^2D - ^2P$ )	$Si + N_2O \rightarrow SiO(a,b) + N_2$ $SiO(a,b) + Na \rightarrow SiO(X) + Na(^2D)$
Na <sub>2</sub> (B-X)	$Br + Na_3 \rightarrow Na_2(B) + NaBr$

Figure 5. Candidate SWCL Systems.

Table I  
NF Spectroscopic and Radiative Properties  
(Reference 424)

State	T (cm <sup>-1</sup> )	w <sub>e</sub> (cm <sup>-1</sup> )	w <sub>e</sub> x <sub>e</sub> (cm <sup>-1</sup> )	B <sub>e</sub> (cm <sup>-1</sup> )	τ (sec)
x <sup>1</sup> Σ	0.0	1141.37	8.99	1.2056	-----
a <sup>1</sup> Δ	11435.16	-----	-----	1.2225	5.6
b <sup>1</sup> Σ	18877.05	1197.49	8.64	1.2377	0.020

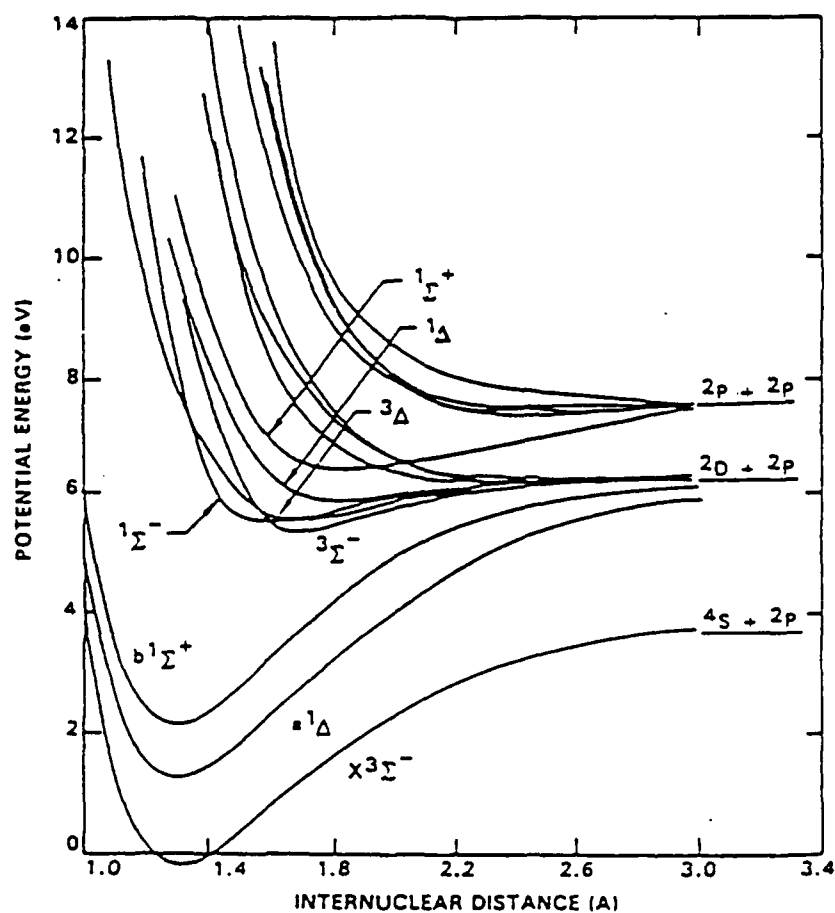


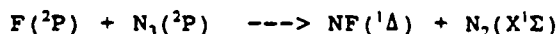
Figure 6. Potential Energy Curves for NF.

Herbelin and Cohen<sup>129</sup> proposed an addition-elimination reaction that directly produces singlet NF:



Malins and Setser,<sup>161</sup> and more recently, Koffend et al<sup>113</sup>, have demonstrated that spin is conserved in the reaction and the branching to the NF(a) product is greater than 91%. The reaction is rapid with a room temperature rate coefficient of  $k = 1.5 \pm 0.2 \times 10^{-11} \text{ cm}^3/\text{molecule-sec.}$ <sup>46</sup> The partitioning to HF(v) and NF products is well characterized.<sup>161</sup> In the presence of excess hydrogen atoms, the singlet NF reacts slowly with H to produce excited nitrogen atoms, N(<sup>2</sup>D), and an NF(a) and N(<sup>2</sup>D) interaction produces electronically excited nitrogen.<sup>47</sup> Thus, the stoichiometry is usually chosen to be lean in hydrogen atoms when excited NF is the desired product. Supersonic flows with NF(a) concentrations as high as  $6 \times 10^{15} \text{ molecules/cm}^3$  have been achieved using this chemistry.<sup>429</sup>

The a<sup>1</sup>Δ state of NF can also be efficiently generated by the reactions of fluorine atoms with hydrogen azide, followed by a second reaction of a fluorine atom with the resulting azide radical:



The rate of NF(a) production is limited by the second reaction with a moderately fast rate coefficient of  $4 \pm 2 \times 10^{-11} \text{ cm}^3/\text{molecule-sec.}$ <sup>378</sup> The yield of NF(a) is high, about 85%. However, this production chemistry does not scale well, as N<sub>3</sub> + N<sub>3</sub> interactions significantly reduce the efficiency of NF(a) production. Indeed, this azide chemistry has been shown to be an efficient source of electronically excited nitrogen.<sup>380</sup>

Benard and coworkers recognized that this scaling limitation might be removed if fluorine azide,  $\text{FN}_3$ , could be used directly. The reaction must proceed through an  $\text{FN}_3$  intermediate and thus one might expect fluorine azide to dissociate to singlet NF products under the proper conditions. Fluorine azide is the most energetic of the halogen azides and is a model for a chemically bound excited state (CBES) material. This energetic compound may be viewed as an  $\text{NF}(a^1\Delta)$  molecule weakly bound to a ground state nitrogen molecule. A potential energy curve for fluorine azide is shown in Figure 7.<sup>16</sup> Only the degree of freedom represented by  $\text{NF}-\text{N}_2$  bond distance is displayed in this figure.

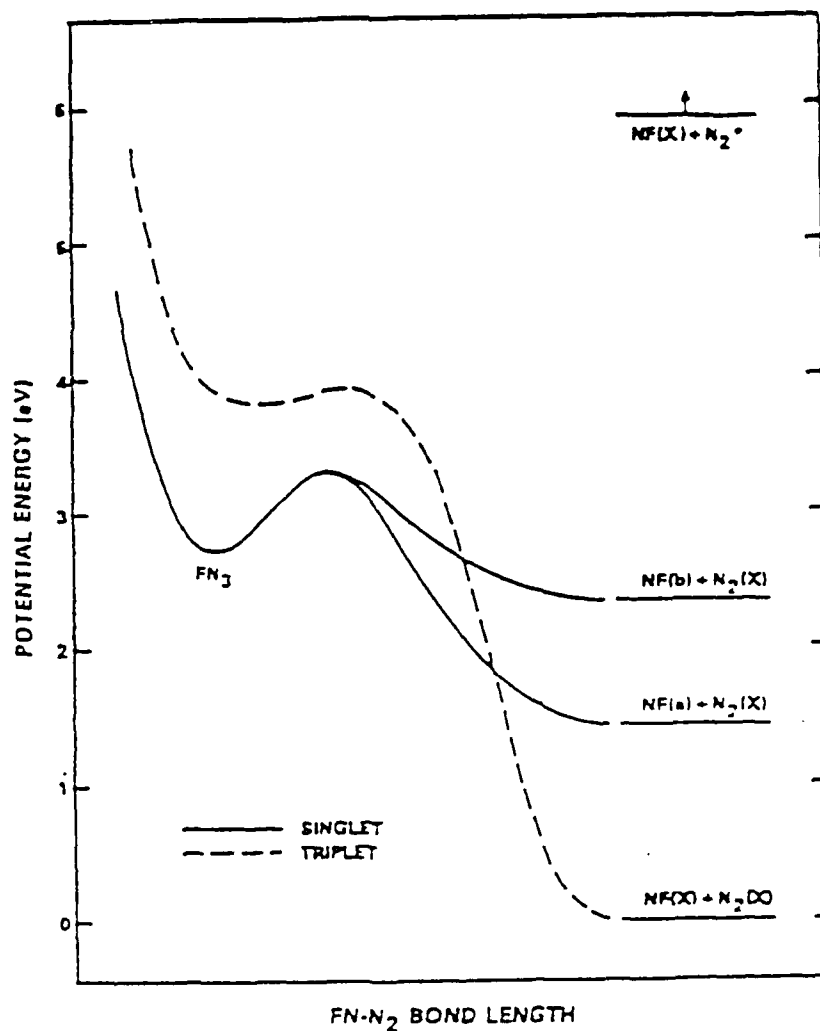


Figure 7. Fluorine azide potential energy curves.

In a pulsed thermolysis experiment where a premixed  $SF_6/FN_3$  gas is rapidly heated by  $CO_2$  laser pumping,  $NF(a^1\Delta)$  concentrations of greater than  $3 \times 10^{16}$  molecules/cm<sup>3</sup> have been achieved with yields of  $70 \pm 25 \%$ .<sup>16</sup>

Clearly, several excellent sources of  $NF(a^1\Delta)$  are currently available. Energy densities on the order of those currently achievable from COIL devices have been demonstrated. Additional scaling of  $NF(a^1\Delta)$  is not required for high power laser development. In addition, at least the  $H + NF_2$  chemistry is highly compatible with existing HF laser hardware and the requisite laser hardware development time may be limited.

The excited singlet states are quite immune to quenching. Setser et al have measured the rates for quenching of  $NF(a)$  and  $NF(b)$  by a wide array of collision partners.<sup>10,42-43,88,103-105</sup> The quenching rate coefficients for  $NF(a)$  by simple molecules rarely exceeds  $10^{-14}$  cm<sup>3</sup>/molecules-sec. Energy pooling reactions often limit the scalability of proposed chemical lasers. There currently exists some uncertainty in the  $NF(a) + NF(a)$  rate. Rate coefficients ranging from less than  $1 \times 10^{-13}$  to  $2.2 \pm 1.2 \times 10^{-12}$  cm<sup>3</sup>/molecule-sec have been reported. Products of this pooling reaction have not been well characterized, but the production of  $NF(b)$  is not a major channel. If the rate coefficient is as large as  $2 \times 10^{-12}$  cm<sup>3</sup>/molecules-sec, energy pooling losses will compete with laser excitation on a time scale of 10-20  $\mu s$  at  $NF(a)$  concentrations of  $3 \times 10^{16}$  molecules/cm<sup>3</sup>. This situation would impose some critical constraints on the system, but would not severely limit high power device scaling.

Methods for extracting the energy stored in singlet  $NF$  in the form of coherent photons, or lasing, are currently under active investigation and are the focus of SWCL program. Only a few efficient receptors of  $NF(a^1\Delta)$  energy have been identified.

Initial work by Capelle et al led to the investigation of bismuth atoms as a receptor of  $\text{NF(a)}$  energy.<sup>40</sup> The energy transfer is near resonant, proceeds at a gas kinetic rate, and would lead to a laser completely analogous to  $\text{O}_2(\text{a})$  pumped  $\text{I}^*$ . In 1983, Herbelin et al attempted to scale the production of  $\text{Bi}(^3\text{D})$  in this system.<sup>128</sup> Upon scaling, the  $\text{Bi}(^3\text{D})$  was efficiently converted to electronically excited bismuth fluoride emitting at 420-480 nm. The scaling of  $\text{BiF(A)}$  with  $\text{NF(a)}$  concentration is shown in Figure 8. These scaling studies have been examined under pulsed, subsonic and supersonic flow conditions and with  $\text{H} + \text{NF}_2$  and  $\text{FN}$ , as the source of  $\text{NF(a)}$ . The scaling depends on bismuth donor.

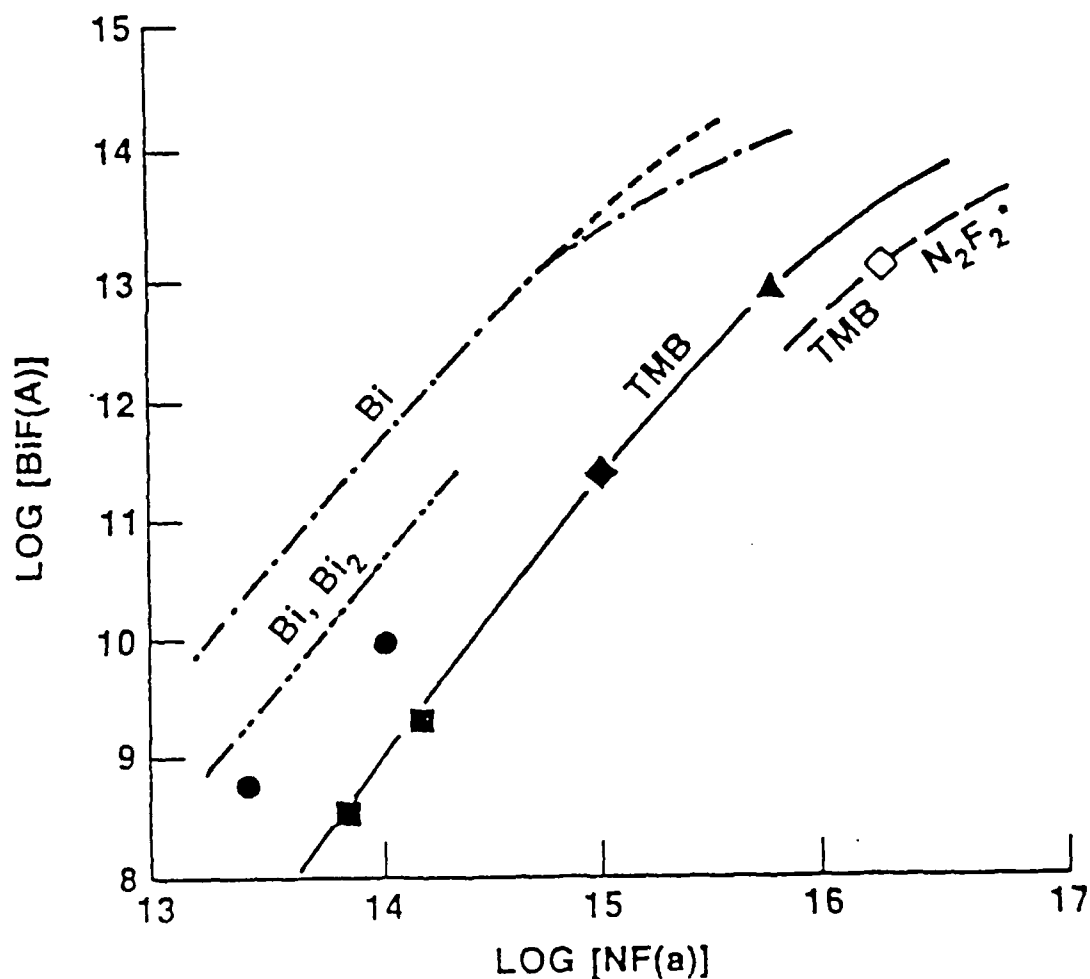


Figure 8.  $\text{BiF(A)}$  Scaling with  $\text{NF(a)}$

#### IV. Status of Current Research Program

The current SWCL program consists of several tasks: (1) obtain saturated lasing in the  $\text{NF(a)}/\text{BiF(A-X)}$  system using shock tube dissociation of fluorine azide, (2) identify and characterize alternatives to  $\text{BiF}$  as the lasant in an excited  $\text{NF}$  driven laser, (3) develop novel methods for delivering atomic bismuth for an  $\text{NF(a)}/\text{BiF(A-X)}$  laser, (4) demonstrate an atomic sodium laser based on energy transfer from metastable  $\text{SiO}$ , (5) demonstrate a sodium dimer laser based on direct reaction of halogen atoms with sodium trimer, (6) investigate the use of vibrational energy in assisting the excitation of an iodine monofluoride laser, (7) demonstrate chemical gain in the  $\text{NCl(b-X)}$  system using excited atomic iodine and  $\text{NCl(a)}$  energy pooling, (8) develop a fully gas phase atomic iodine chemical laser based on energy transfer from  $\text{NCl(a)}$ , and (9) identify and characterize novel metastable energy carriers such as electronically excited  $\text{PF}$ .

As previously discussed, the thermal dissociation of fluorine azide,  $\text{FN}_3$ , is an efficient source of  $\text{NF(a}^1\Delta)$  at concentrations greater than  $3 \times 10^{16}$   $\text{cm}^3/\text{molecule-s}$ . This process may be rapidly initiated by a Mach 2.5 shock wave passing through fluorine azide dilute in He. By seeding trace amounts of  $\text{Bi}(\text{CH}_3)_3$ , (TMB) into the shocked gas mixture, electronically excited  $\text{BiF(A)}$  at concentrations of  $7 \times 10^{13}$   $\text{molecules}/\text{cm}^3$  have been achieved. Using a gain length of less than 50 cm, weak lasing on the  $\text{BiF(A-X, 1-4)}$  band at 470 nm has been achieved. The gain is low and the system is inefficient due to quenching of  $\text{NF(a)}$  by TMB. Either an alternate bismuth donor or alternate laser specie is required for efficient  $\text{NF(a)}$  energy extraction. One promising alternative lasant specie is  $\text{BH(A}^1\Pi)$ , which is rapidly produced by sequential energy transfer from  $\text{NF(a)}$ .

Three distinct measurements of optical gain exceeding 1% have recently been reported for the atomic sodium  $4d\ ^3D - 3p\ ^2P$  transition which is excited

by energy transfer from metastable electronic states of SiO. Subsonic flows of sodium ( $10^{20}$  atoms/cm<sup>2</sup>-s) and SiO (produced from Si + N<sub>2</sub>O) intersecting at 90° with a path length of 5 cm establish a CW gain of 0.1 cm<sup>-1</sup> at  $\lambda=569$  nm. For an optical cavity with 0.2% output coupling, the steady output intensity exceeds 10<sup>3</sup> times that for the same cavity with the high reflector blocked. Furthermore, a scanning ring dye laser gain probe has independently established a gain of 1.5%/pass.

The data base for developing a Short Wavelength Chemical Laser is quite mature, particularly for NF(a) based systems. The recent reports of chemically produced gain and lasing in the visible are quite exciting. Once efficient, saturated lasing is achieved, a more aggressive program to develop a fully CW, high power chemical laser should be pursued.

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A CHEMICAL PROCESS YIELDING STIMULATED EMISSION OF VISIBLE RADIATION VIA FAST NEAR RESONANT ENERGY TRANSFER

Georgia Tech. Research Corporation

Patent: PCT International, WO 9008414 A1, 900726, Appl # WO 90US255 (900110) \*US 37504 (870330) \*US 296512 (890112) \*US 373043 (890703), 47 pp; 1990

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A PURELY CHEMICAL PROCESS YIELDING CONTINUOUS LASER AMPLIFICATION IN THE VISIBLE AND ULTRAVIOLET SPECTRAL RANGES

Georgia Tech. Research Corp.

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Georgia Tech Research Corporation

Patent # US 5020071 A, 910528, Appl. # US 375043 (890703) \*US 296512 (890112), 15 pp, Cont. of U.S. Ser. # 296, 512; 1991

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13. ABSTRACT (Maximum 200 words) <p>High power short wavelength chemical laser (SWCL) systems offer great advantages for strategic and tactical military applications, including both weapons and imaging missions. The promise of very high brightness, high mass efficiency and wavelength agility has justified a modest basic research program for more than a decade. Significant progress towards the demonstration of a visible chemical laser has been made during the past few years. Highly efficient methods of chemically producing metastable electronic states at concentrations exceeding <math>3 \times 10^{16}</math> molecules/cm<sup>3</sup> have been developed. Energy transfer from these metastables to suitable lasing species has been used to demonstrate gain in the visible. Chemically generated gain of 0.029 %/cm on the (A-X) electronic transition in bismuth fluoride has been demonstrated using pulsed thermolysis of fluorine azide and trimethylbismuth mixtures. Recently, a table-top shock facility has been used to achieve unsaturated lasing in the same system. During the past ten years, over 400 articles and reports have resulted from this research program. This bibliography summarizes this Department of Defense sponsored research on Short Wavelength Chemical Lasers since 1980.</p>				
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